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	63Y	678	802	804	80Y		
C2C	20Y	311	31Y	360	361	362	364 36Y
	498	500	50Y	606	623	624	633 643
	644	771	772	798	79Y	YB	
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(54) PROCESS FOR THE PREPARATION OF A PHOTOGRAPHIC MATERIAL

(71) We, KONISHIROKU PHOTO INDUSTRY CO. LTD., a Japanese Body Corporate of 1-10, 3-Chome, Nihonbashi-Muro-Machi, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for the preparation of photographic materials, and specifically, a process for improving the coating thereof to form a uniform film as a structural layer of the photographic material.

As is well known, a photographic material comprises a support such as glass plate, baryta paper, polyethylene-laminated paper, nitrocellulose, cellulose acetate, polyester or polycarbonate, which support is coated with a subbing layer, a photosensitive emulsion layer, a protective layer, a filter layer, and an anti-halation layer. Usually, these layers are coated on the support by way of a dipping method, a double roll method or a slide hopper method, followed by drying, using coating devices. It is important to coat these various coating liquids for photography over the whole of the surface of the support to a uniform thickness.

Coating defects observed when various photographic coating liquids are directly applied on the support tend to be different from coating defects observed when a coating liquid is applied on an already-coated layer, depending on whether the coated layer is dry or in a cold-set state, and from those observed when two or more liquids are coated at the same time. This is because the surface condition differs greatly; the above-mentioned defects differ depending on the conditions. Thus, it is quite important for the formation of a uniform coating to place the coating liquid in a uniform wet state, regardless of the surface conditions.

In conventional coating processes, however, coating irregularities are often found; these are called "lateral irregularities" or "longitudinal irregularities", which are respectively formed perpendicular to or parallel with the coating direction. In addition, a partly incomplete coated state, referred to as "comets", is sometimes found resulting from foreign matter such as small amounts of dirt and dust, insoluble materials, coagulated materials and oleophilic materials which are present on the surface to be coated or are present in a coating liquid. Non-uniform coating called as "slippage" or "cutout" is also sometimes observed causing relatively thick areas or, conversely, relatively thin areas as the coating liquid collects near the periphery of the coated surface or disperses away from the periphery of the coated surface.

Therefore, to prevent such non-uniformity in the coating layer, it has been usual to employ a coating aid such as saponin to lower the surface tension of the coating liquid. However, a saponin of natural origin is of inconsistent quality. Moreover, even if the saponin of the same quality is used, great variations are inevitable with regard to photographic properties as well as coating properties.

Therefore, various synthetic surfactants have been used as coating aids in place of saponin.

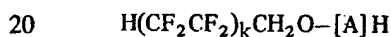
nin. In practice, however, the conventional synthetic surfactants tend to cause certain photographic properties, particularly storageability under the conditions of high temperature and high humidity, to deteriorate or they lack high speed coating performance. Thus, the surfactants are effective only for specific photographic coating liquids or only under

5 limited coating conditions and are not applicable for general purposes.

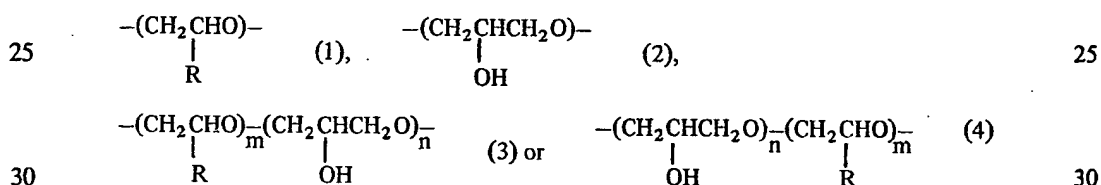
An object of the present invention is to provide a process for the preparation of light-sensitive photographic materials which have uniform coatings free from deficiencies such as irregularities, comets, cissing, even when a variety of photographic coating liquids with or without various photographic binders such as gelatin are coated by high speed coating. The

10 coating aids used should be capable of giving good wet state uniformity when a variety of photographic coating liquids are being coated using a simultaneous multi-layer coating system. The light-sensitive photographic materials produced should provide stable, reproducible photographic properties, while having good wettability to processing liquids and showing no foaming in high speed automatic processing or development.

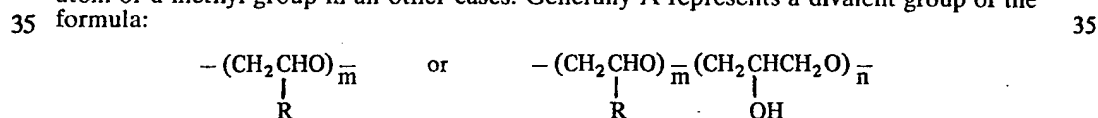
15 We have found, according to the present invention, that these objects can generally be attained when a compound represented by the following general formula is added as a coating aid to a variety of photographic coating liquids, in preparing the photographic materials for use in photography:



where A represents a divalent group of formula:



k representing an integer of 2 to 10, each of m and n representing an integer from 1 to 50, and R representing a methyl group in formulae (3) and (4) when n is 1, and a hydrogen atom or a methyl group in all other cases. Generally A represents a divalent group of the



40 Accordingly the present invention provides a process for the preparation of a photographic material comprising a support carrying at least one layer thereon, which process comprises applying a said layer by coating with a liquid which contains at least one compound of formula (I).

The compound of formula (I) exhibits excellent surfactant effects and gives no noticeable adverse effects on the photosensitive emulsion. Among the compounds especially preferred are those when A represents $\text{-(CH}_2\text{CH}_2\text{O)-}$, k is 2 or 3 and m is an integer of 5 to 20 inclusive. A represents $\text{-(CH}_2\text{CH(OH)CH}_2\text{O)-}$, n is an integer of 5 to 20 inclusive and k is 2 or 3. Compounds in which k is less than 2 do not possess sufficiently good surfactant properties.

50 Further, the compounds of formula (I) are not unstable as is saponin, but reduces the surface tension even when used in small amounts without increasing the viscosity of the coating liquids. Therefore, by using the compounds of formula (I), irregularities and comets can be avoided when coating at ordinary speed or even when coating at speeds as high as 40 metres per minute or when the coating liquid contains a small amount of a binder such as gelatine, or even when a multi-layer is coated; it is possible to form a very uniform coating and to provide very stable and consistent coating properties.

In addition to improving the coating properties, the compound of formula (I) provide other advantages, such as imparting antistatic properties to the photographic materials as well as preventing static marks, when the compound is contained in a protective layer, a

60 The compounds of formula (I) are surfactants containing fluorine atoms and exhibit surfactant effects superior to the conventional compounds having similar structures but which are not substituted by fluorine atoms. Therefore, it is possible to use the compounds of formula (I) in all or some of the multi-layered coatings coated one above another on the same support, which coatings are prepared by a wet-on-wet method or a wet-on-dry

Moreover, the compounds of formula (I) have excellent wetting properties since foaming in the coating liquid is prevented; therefore, the compounds do not cause bubbles when contacted with a processing liquid during the treatment of the photographic material.

	Exemplified compound	n ³⁰ _D	
10	(1) H(CF ₂ CF ₂) ₂ CH ₂ O(CH ₂ CH ₂ O) ₅ H	1.3852	10
	(2) H(CF ₂ CF ₂) ₂ CH ₂ O(CH ₂ CH ₂ O) ₁₀ H	1.4056	
15	(3) H(CF ₂ CF ₂) ₂ CH ₂ O(CH ₂ CH ₂ O) ₂₀ H	1.4431	15
	(4) H(CF ₂ CF ₂) ₃ CH ₂ O(CH ₂ CH ₂ O) ₁₀ H	1.3774	
	(5) H(CF ₂ CF ₂) ₄ CH ₂ OCH ₂ CH ₂ OH	1.3350	
20	(6) H(CF ₂ CF ₂) ₄ CH ₂ O(CH ₂ CH ₂ O) ₁₀ H	1.3387	20
	(7) H(CF ₂ CF ₂) ₃ CH ₂ O(CH ₂ CH ₂ O) ₅ H	1.3774	
	(8) H(CF ₂ CF ₂) ₃ CH ₂ OCH ₂ CH ₂ OH	1.3376	
25	(9) H(CF ₂ CF ₂) ₂ CH ₂ OCH ₂ CH ₂ OH	1.3412	25
	(10) H(CF ₂ CF ₂) ₂ CH ₂ O(CH ₂ CH(OH)CH ₂ O) ₅ H	1.4427	
30	(11) H(CF ₂ CF ₂) ₃ CH ₂ O(CH ₂ CH(OH)CH ₂ O) ₈ H	1.4462	30
35	(12) H(CF ₂ CF ₂) ₂ CH ₂ O(CH ₂ CH(OH)CH ₂ O) ₇ H	1.4542	35
40	(13) H(CF ₂ CF ₂) ₃ CH ₂ O(CH ₂ CH(OH)CH ₂ O) ₃ H	1.3975	40
	(14) H(CF ₂ CF ₂) ₂ CH ₂ O(CH ₂ CH(OH)CH ₂ O) ₃ H	1.4193	
45	(15) H(CF ₂ CF ₂) ₂ CH ₂ OCH ₂ CH(OH)CH ₂ OH	1.3703	45
50	(16) H(CF ₂ CF ₂) ₃ CH ₂ OCH ₂ CH(OH)CH ₂ OH	1.3632	50
55	(17) H(CF ₂ CF ₂) ₄ CH ₂ O(CH ₂ CH(OH)CH ₂ O) ₁₀ H	1.3329 (1% aq.)	55
60	(18) H(CF ₂ CF ₂) ₈ CH ₂ O(CH ₂ CH ₂ O) ₄₀ H	1.4126 (1% aq.)	60
65	(19) H(CF ₂ CF ₂) ₁₀ CH ₂ O(CH ₂ CH ₂ O) ₅₀ H	1.4562 (1% aq.)	65

	(20) $\text{H}(\text{CF}_2\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2\underset{\text{OH}}{\text{CHCH}_2\text{O}})_{30}\text{H}$	1.4462	
		(1% aq.)	
5	(21) $\text{H}(\text{CF}_2\text{CF}_2)_8\text{CH}_2\text{O}(\text{CH}_2\underset{\text{OH}}{\text{CHCH}_2\text{O}})_{40}\text{H}$	1.4366	5
		(1% aq.)	
10	(22) $\text{H}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{O}(\text{CH}_2\underset{\text{CH}_3}{\text{CHO}})_{10}\text{H}$	1.4458	10
	(23) $\text{H}(\text{CF}_2\text{CF}_2)_6\text{CH}_2\text{O}(\text{CH}_2\underset{\text{CH}_3}{\text{CHO}})_{10}(\text{CH}_2\underset{\text{OH}}{\text{CHCH}_2\text{O}})_{50}\text{H}$	1.4631	
15		(1% aq.)	15
	(24) $\text{H}(\text{CF}_2\text{CF}_2)_8\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_5(\text{CH}_2\underset{\text{OH}}{\text{CHCH}_2\text{O}})_{20}\text{H}$	1.4275	
		(1% aq.)	
20	(25) $\text{H}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{O}(\text{CH}_2\underset{\text{OH}}{\text{CHCH}_2\text{O}})_3(\text{CH}_2\text{CH}_2\text{O})_{13}\text{H}$	1.4434	20
25	(26) $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{O}(\text{CH}_2\underset{\text{OH}}{\text{CHCH}_2\text{O}})_{20}(\text{CH}_2\underset{\text{CH}_3}{\text{CHO}})_5\text{H}$	1.4362	25
		(1% aq.)	

Synthesis Example 1 (Synthesis of Exemplified compound (1)):

30 0.1 Mole of $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OH}$, 1 ml of a 50% sodium hydroxide aqueous solution, and 30
0.5 mole of ethylene oxide are introduced into a pressure-resistant glass reaction tube or
into a stainless steel autoclave, and heated for 3 hours at 90°C. The resulting mixture is
thereafter neutralized with glacial acetic acid, and then filtered. The excess glacial acetic
acid is removed under reduced pressure to obtain the compound.

35 $n_D^{30} = 1.3852$ 35

Synthesis Example 2 (Synthesis of Exemplified compound (2)):

40 0.1 Mole of $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OH}$, 1 ml of a 50% sodium hydroxide aqueous solution, and 40
1.0 mole of ethylene oxide are introduced into a pressure-resistant glass reaction tube or
into a stainless steel autoclave, and heated for 3 hours at 90°C. The operation thereafter is
the same as that of Synthesis Example 1. $n_D^{30} = 1.4056$

Synthesis Example 3 (Synthesis of Exemplified compound (3)):

45 0.05 Mole of $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OH}$, 1 ml of a 50% sodium hydroxide aqueous solution, 45
and 1.0 mole of ethylene oxide are introduced into a pressure-resistant glass reaction tube
or into a stainless steel autoclave, and heated for 6 hours at 90°C. The operation thereafter
is the same as that of Synthesis Example 1. $n_D^{30} = 1.4431$

Synthesis Example 4 (Synthesis of Exemplified compound (4)):

50 0.1 Mole of $\text{H}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{OH}$, 1 ml of a 50% sodium hydroxide aqueous solution and 50
1.0 mole of ethylene oxide are introduced into a pressure-resistant glass reaction tube or
into a stainless steel autoclave, and heated for 3 hours at 90°C. The operation thereafter is
the same as that of Synthesis Example 1. $n_D^{30} = 1.3774$

Synthesis Example 5 (Synthesis of Exemplified compound (5)):

55 0.1 Mole of $\text{H}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{OH}$, 30 ml of acetone, 1 ml of a 50% sodium hydroxide 55
aqueous solution, and 0.1 mole of ethylene oxide are introduced into a pressure-resistant
glass reaction tube or into a stainless steel autoclave, and heated for 3 hours at 90°C, and
thereafter neutralized with glacial acetic acid. The solvent is removed under reduced pres-
sure. The remainder is distilled under reduced pressure to obtain the compound. Boiling
point, 92° - 105°C/3 mmHg, $n_D^{30} = 1.3350$

60 Synthesis Example 6 (Synthesis of Exemplified compound (6)):

0.1 Mole of $\text{H}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{OH}$, 30 ml of acetone, 1 ml of a 50% sodium hydroxide
aqueous solution and 1.0 mole of ethylene oxide are introduced into a pressure-resistant
glass reaction tube or into a stainless steel autoclave, and heated for 3 hours at 90°C. The
operation thereafter is the same as that of Synthesis Example 1. $n_D^{30} = 1.3387$

65 Synthesis Example 7 (Synthesis of Exemplified compound (10)):

In a flask equipped with a stirrer and a thermometer, 0.2 gram of potassium hydroxide is dissolved in 0.2 mole of $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OH}$, and to the resulting solution is dropwise added 0.1 mole of glycidol, while maintaining the interior temperature at 130°C . After the dropwise addition has been completed, the mixture is heated for 4 hours and stirred. After cooling, the mixture is neutralized with glacial acetic acid, thereafter dissolved in a mixture solution of water and methanol (2:3), and extracted with a petroleum ether. The water-methanol layer is evaporated to dryness to obtain a faintly yellow viscous liquid.

$n_D^{30} = 1.4427$

Synthesis Example 8 (Synthesis of Exemplified compound (11)):

In a flask equipped with a stirrer and a thermometer, 0.2 g of a potassium hydroxide is dissolved in 0.1 mole of $\text{H}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{OH}$, and to the resulting solution is slowly and dropwise added 0.8 mole of glycidol, while maintaining the interior temperature at 130°C . After the dropwise addition has been completed, the mixture is heated for 4 hours and stirred. After cooling, the mixture is neutralized with glacial acetic acid, dissolved in a mixture of water and methanol (2:3), and extracted with a petroleum ether. The water-methanol layer is evaporated to dryness to obtain a faintly yellow viscous liquid. $n_D^{30} = 1.4462$

Synthesis Example 9 (Synthesis of Exemplified compound (12)):

In a flask equipped with a stirrer and a thermometer, 0.2 g of a potassium hydroxide is dissolved in 0.1 mole of $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OH}$, and to the resulting solution is slowly added 0.7 mole of glycidol, while maintaining the interior temperature at 130°C . After the dropwise addition has been completed, the mixture is heated for 4 hours and stirred. After cooling, the mixture is neutralized with glacial acetic acid, dissolved in a mixture of water and methanol (2:3), and extracted with a petroleum ether. The water-methanol layer is evaporated to dryness to obtain a faintly yellow viscous liquid. $n_D^{30} = 1.4542$

Synthesis Example 10 (Synthesis of Exemplified compound (22)):

0.1 Mole of $\text{H}(\text{CF}_2\text{CF}_2)_3\text{CH}_2\text{OH}$, 2 ml of a 50% sodium hydroxide aqueous solution, and 1.0 mole of propylene oxide are introduced into a pressure-resistant glass reaction tube or into a stainless steel autoclave, and heated at 110° to 120°C for 6 hours. After cooling, the reaction mixture is neutralized with glacial acetic acid to obtain a colorless viscous liquid. $n_D^{30} = 1.4458$

Synthesis Example 11 (Synthesis of Exemplified compound (25)):

In a flask equipped with a stirrer and a thermometer, one mole of $\text{H}(\text{CF}_2\text{CF}_2)_4\text{CH}_2\text{OH}$ and 0.2 g of potassium hydroxide are dissolved in 100 ml of xylene and stirred violently, and to the resulting solution is slowly and dropwise added 3 mole of glycidol with refluxing. After the dropwise addition has been completed, the mixture is stirred for 4 hours under refluxing. After cooling, the mixture is neutralized with glacial acetic acid, freed from xylene, and then dissolved in alcohol. The solution is filtered, and the filtrate is evaporated to dryness to obtain a white waxy product.

0.5 Mole of the waxy product so obtained and 0.5 g of potassium hydroxide are dissolved in 300 ml of xylene, and stirred with refluxing. Into the resulting solution is slowly blown 12.5 mole of ethylene oxide. After the completion of the reaction, confirmed by the weight increase, the reaction product is neutralized with glacial acetic acid and freed from xylene. The product is dissolved in alcohol, filtered, and then evaporated to dryness to obtain a brown viscous liquid. $n_D^{30} = 1.4434$

In order to add the compound of formula (I) to the photographic coating liquids, the compound may be dissolved in an water-miscible organic solvent such as water or methanol, ethanol, or acetone. The amount of the compound added to the coating liquid is generally 0.01 to 20 g per kilogram of the coating liquid if the liquid contains ordinary gelatine, and more preferably 0.05 to 10 g. Also, the addition is usually made just before the liquid is coated. But in the case of a silver halide emulsion, the compound can be added at any time during the aging step.

Layers in the light-sensitive photographic material of the present invention include not only a light-sensitive silver halide emulsion layer but also, for example, an intermediate layer, a protective layer, a subbing layer, a filter layer, an anti-halation layer, and an overcoat layer. Examples of silver halide emulsions to be used include a variety of photosensitive emulsions that are usually used for black-and-white emulsions, colored emulsion, X-ray emulsions, lith-type emulsions, diffusion-transfer emulsions, and subtractive emulsions. The emulsions may contain a variety of silver halides such as silver chloride, silver bromochloride, silver iodobromochloride, silver bromide, silver iodobromide, etc.

In carrying out the present invention, the most typical silver halide emulsion is a gelatinous silver halide emulsion; other examples may be silver halide emulsions comprising acetylated gelatine, phthalated gelatine, or water-soluble cellulose derivatives, polyvinyl alcohol, or other hydrophilic synthetic or naturally-occurring high-molecular compounds as binder.

These emulsions may contain chemical sensitizer noble metal sensitizers such as gold compounds, palladium compounds, platinum compounds, rhodium compounds, iridium compounds, active or non-active selenium compounds, or sulfur sensitizers such as sodium thiosulfate, or may further contain development accelerators such as thioether compounds, quaternary ammonium salts, or polyalkylene oxide compounds. Particularly preferred compounds are those disclosed in Japanese Patent Publication No. 13822/68, and Japanese Patent Publication No. 11116/72. The emulsions can be stabilized using azoles, azaindenes, and mercaptotetrazoles. The emulsions may further contain dihydroxyalkanes, cyclohexanediols, acetylene alcohols, or wetting agents, plasticizers, or compounds for improving physical properties of coatings such as water-dispersible granular high molecular compounds obtained by emulsion polymerization. Furthermore, as a coating hardening agent, there may also be used, for example, aldehydes, ethylene imines, ketones, carboxylic acid derivatives, sulfonic esters, sulfonyl halides, vinyl sulfonates, active halogen compounds, epoxy compounds, isocyanates, and carbodiimides.

To the compositions used in the process of the present invention, there may also be added conventional surfactants such as saponin, or, for example, surfactants of the sulfosuccinic acid type disclosed in British Patent Specification No. 548532, surfactants of the alkylaryl polyethersulfonate type disclosed in U.S. Patent Specification No. 3,026,202, or anionic or non-ionic surfactants of the alkylaryl polyether alcohol type, or ampholytic surfactants containing ammonium- or phosphonium-type cations and carboxylate- or sulfonate-type anions, such as are disclosed in Japanese Early Publication Nos. 3219/76, 32322/76 and 46733/74. Furthermore, the emulsions may contain hydrophilic and oleophilic couplers, various dyes and dye carriers, or antistatic agents (for example, ethylene oxide addition polymers or glycidol addition polymers, phenol aldehyde condensates, or aliphatic amines and amides, as disclosed in Japanese Early Publication No. 19213/73, and Japanese Patent Early Publication No. 74929/74), as well as various photographic additives such as optical brighteners, UV-absorbers, antistain agents, matting agents, development inhibitors, and antioxidants. These additives may also be employed even when the compound of formula (I) is contained in layers other than the emulsion layer. The emulsion may be further increased with respect to spectral sensitivity by using, if necessary, cyanine dyes, merocyanine dyes, and styryl dyes.

The following is a Test Example to show that the compound of formula (I) is very effective for minimizing the surface tension of a coating liquid, in which the compound of formula (I) is added to a gelatine solution to measure the surface tension:

Test Example:

To 5% gelatine solutions were added the Exemplified compounds (7) and (11), and saponin as a comparative compound, in amounts of 0.6 g and 1.2 g per kilogram of gelatine solution. These solutions and the 5% gelatine solution to which the compound was not added were measured for their surface tension (37°C, dyne/cm). The results were as shown in Table 1 below.

Table 1

Compound added	Amount added (in gram per kg of 5% gelatine solution)	Surface tension dyne/cm (37°C)
—	—	49
Exemplified compound (7)	0.6	29
	1.2	27
Exemplified compound (12)	0.6	30
	1.2	29
Saponin	0.6	42
	1.2	39

As will be apparent from Table 1 above, the compounds of formula (I) serve to markedly reduce the surface tension of the solution, this being far superior to the saponin (employed in conventional processes).

Therefore, the resulting coating is uniform and does not adversely affect the photographic properties. Thus, the compound of formula (I) exhibits excellent properties as a surfactant.

The present invention is illustrated further in the following Examples.

Example 1

A silver bromochloride emulsion (containing 80 mole % of silver chloride) with 6% gelatine was separated into eight groups. To six samples were respectively added, as an aqueous solution, the exemplified compounds (2), (4) and (13) in amounts of 2 g and 4 g per kilogram of the emulsion.

To a further sample was added saponin, as a comparative example, in an amount of 4 g per kilogram of the emulsion, and a further sample containing no added compound was used as a blank. The resulting eight emulsions were coated on a baryta paper at a speed of 40 meters per minute to prepare light-sensitive photographic positive materials.

After drying, each of these samples were measured for their coating and photographic properties. The results are as shown in Table 2. The sensitometry was performed after the exposure with a KS-IV-type sensitometer (manufactured by Konishiroku Photo Industry Co., Ltd.) following standard treatment using a developer D-72 (product from Eastman Kodak Co.). The relative speed in the Table represents a relative value with the speed of the blank sample as 100.

Table 2

Compound added	Amount added (g/kg of emulsion)	Coating property		Photographic property	
		Number of repellencies (No./10m ²)	Number of comets (No./10m ²)	Relative speed	Fog
—	—	34	12	100	0.03
Exemplified compound (2)	2.0	0	0	100	0.03
	4.0	0	0	100	0.03
Exemplified compound (4)	2.0	0	1	100	0.03
	4.0	0	0	100	0.03
Exemplified compound (14)	2.0	1	0	100	0.04
	4.0	0	0	100	0.04
Saponin	4.0	3	1	100	0.04

As will be apparent from Table 2, the compounds of formula (I) exhibit excellent coating properties when coated at high speed with very little repellencies and comets, and give no adverse effects on the photographic properties.

A silver iodobromide emulsion containing 5% of gelatine (containing 2 mole % of silver iodide) was prepared for high speed X-ray photographic use. The emulsion was divided into twelve groups, and to ten groups were respectively added the exemplified compounds (1), (4), (7), (11) and (16) in amounts of 3 g and 5 g, per kilogram of emulsion. The resulting solutions were coated at a speed of 40 metres per minute on polyester films which had been subbed. The films were set by cooling, and were then coated with 2.5% gelatin solutions each containing said exemplified compounds corresponding to the compounds used in the emulsions in an amount of 2 g per kilogram of the coating solution, as a protective layer and at the same coating speed. To the remaining two groups was similarly added a p-t-octyl-phenylpolyethylene glycol ether (comparative compound A), and the solutions were coated to form an emulsion layer and a protective layer, thereby obtaining comparative samples.

The results of the coated samples are shown in Table 3 below. The relative speed in the Table is a relative value with the speed of the sample having a coating in which was added 3g of the comparative compound A per kilogram of the emulsion, as 100.

Table 3

5	Compound added	Emulsion layer added (g/kg emulsion)	Protective layer added (g/kg.25% gelatine)	Coating property		Photographic property		5
				Number of repellencies (No./10m ²)	Number of comets (No./10m ²)	Relative speed	Fog	
10	Exemplified compound (1)	3.0	2.0	0	1	100	0.07	10
		5.0	2.0	0	0	100	0.07	
	Exemplified compound (4)	3.0	2.0	0	0	100	0.08	
		5.0	2.0	0	0	97	0.07	
15	Exemplified compound (7)	3.0	2.0	0	0	100	0.08	15
		5.0	2.0	0	0	100	0.07	
20	Exemplified compound (11)	3.0	2.0	0	0	100	0.07	20
		5.0	2.0	0	0	100	0.07	
	Exemplified compound (16)	3.0	2.0	1	0	100	0.08	
		5.0	2.0	0	0	100	0.07	
25	Comparative compound A	3.0	2.0	4	3	100	0.08	25
		5.0	2.0	2	2	98	0.09	

As will be clear from the results of Table 3 above, the coating containing the comparative compound is defective, whereas the samples containing the compounds of formula (I) hardly develop any defects such as repellencies and comets when coated over other coatings.

Example 3

A biaxially oriented polyethylene terephthalate film was subbed and then coated with the same high speed silver halide emulsion for X-ray photography as used in Example 2 and with a protective layer-forming solution (the two solutions containing saponin as a surfactant). The resulting film was divided into several portions and on which were overcoated the solutions of 0.5 g of the exemplified compounds (4), (7) and (12) and 100 ml of pure methanol, and the samples were dried at 30°C for 3 minutes.

It was confirmed that the methanol solutions containing the compounds of formula (I) exhibit excellent properties as compared to the methanol solution without the compounds. The films overcoated with these solutions were superposed on a sensitizing screen for X-ray in a dark room, and then subjected to a pre-determined amount of abrasion from the brightening paper side using a rubber roller under a relative humidity of 30%, and then developed to examine static marks. The film treated with the methanol solution not containing the compound of formula (I) caused noticeable static marks over the entire surface, whereas the films treated with the solutions containing the compounds of formula (I) did not show static marks at all.

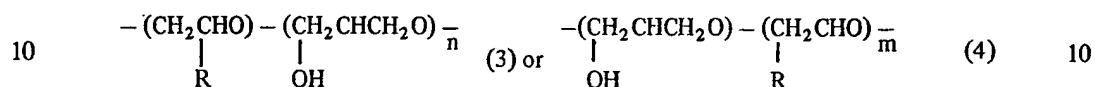
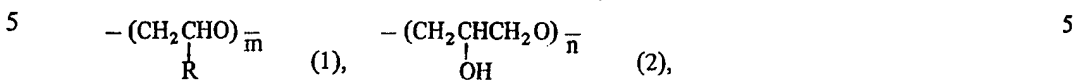
The same test was carried out on the samples of Examples 1 and 2. It was confirmed that the samples containing the compounds of formula (I) showed less static marks than the comparative samples.

WHAT WE CLAIM IS:-

1. A process for the preparation of a photographic material comprising a support carrying at least one layer thereon, which process comprises applying a said layer by coating with a liquid which contains at least one compound of general formula:



where A represents a divalent group of formula:



15 k representing an integer of 2 to 10, each of m and n representing an integer from 1 to 50, and R representing a methyl group in formulae (3) and (4) when n is 1, and a hydrogen atom or a methyl group in all other cases. 15

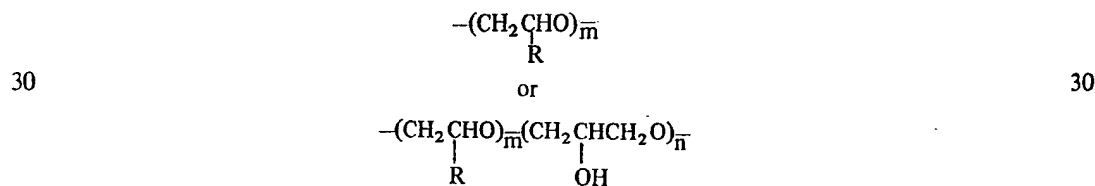
2. A process according to claim 1 wherein the layer is a photosensitive emulsion layer containing silver halide.

20 3. A process according to claim 2 wherein the material further comprises a protective layer. 20

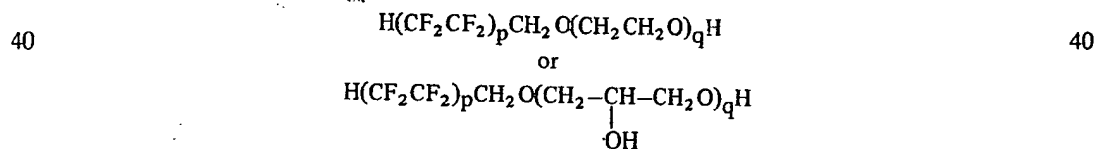
4. A process according to claim 1 wherein the layer is a protective layer, the material further comprising a photosensitive emulsion layer containing silver halide.

5. A process according to any one of claims 1 to 4 wherein the liquid further contains an anionic surfactant.

25 6. A process according to any one of the preceding claims wherein A represents a divalent group of formula: 25

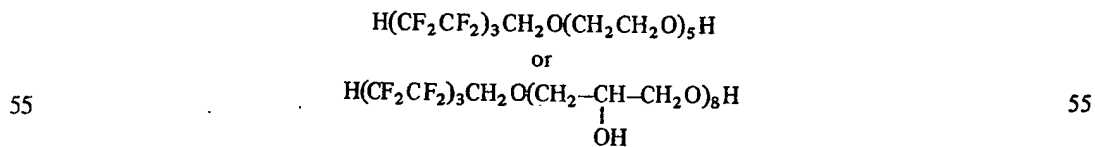


35 7. A process according to claim 6 wherein the compound is represented by the following formulae: 35



45 wherein p is 2 or 3 and q is an integer of 5 to 20 inclusive. 45

50 8. A process according to claim 7 wherein the compound is: 50



60 9. A process according to any one of claims 1 to 7 wherein the compound is any one or more of those hereinbefore set forth as exemplified compounds (1) to (6), (7) to (11) and (13) to (26). 60

10. A process according to claim 1 substantially as described in any one of the Examples.

65 11. A photographic material whenever produced by a process as claimed in any one of claims 1 to 5, 7 and 10. 65

12. A photographic material whenever produced by a process as claimed in any one of claims 6, 8 and 9.

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